

Applicability of coumarin for detecting and measuring hydroxyl radicals generated by photoexcitation of TiO₂ nanoparticles

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Received 7 September 2007; received in revised form 21 December 2007; accepted 2 January 2008

Available online 12 January 2008

Abstract

Applicability of coumarin (COU) as fluorescent probe to detect and measure hydroxyl radicals generated by UV irradiation of aqueous suspension of TiO₂ was investigated under aerobic and anaerobic conditions. The fluorescent 7-hydroxycoumarin (7HC) was formed in argon-saturated suspension when silver ion was used as electron acceptor. The luminescence intensity increased with irradiation time until the deposition of silver on the surface of TiO₂ was completed and then the luminescence intensity was constant and proportional to the initial concentration of the silver ion. The low yield of 7HC related to the deposited silver (0.32%) indicates the appearance of efficient side reactions of hydroxyl radicals and holes. It has also been demonstrated that efficient electron donors reacting directly with photogenerated holes such as oxalic acid significantly reduce the yield of 7HC. Using oxalic acid of relatively high concentration in aerated suspension leads to the production of hydroxyl radical in thermal reactions followed by primary electron transfer steps.

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Keywords: Heterogeneous photocatalysis; TiO₂; Hydroxyl radical; Coumarin; Fluorescent probe

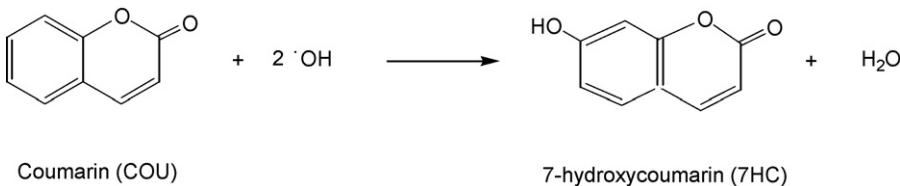
1. Introduction

In recent years considerable attention has been devoted to reveal the details of TiO₂ photocatalysis because the procedures based on the application of this semiconductor have been proved to be efficient for decomposition and mineralization of various organic and inorganic pollutants contaminating air, wastewater and drinking water [1–7]. When a TiO₂ particle is exposed to photon of sufficient energy ($h\nu > E_{bg}$; $E_{bg} = 3.23$ eV for anatase, and $E_{bg} = 3.02$ eV for rutile) [8] the energy of photon is absorbed and an electron is promoted from the valence band into the conduction band. This movement of electron leaves a hole in the valence band. Under aerobic conditions the conduction band electron is trapped by adsorbed oxygen molecule with a relatively high quantum yield, producing $O_2^{\bullet-}$ ion which is readily protonated in acidic media [9]. On the other hand the photon-generated hole, in the absence of reducing species, converts the surface adsorbed water or hydroxide ion into a hydroxyl radical [10].

Hydroxyl radical can also be formed by thermal reactions following the primary electron transfer processes occurring at the surface of semiconductor particles or in the liquid phase. Furthermore, hydrogen peroxide is produced by reactions of $O_2^{\bullet-}$ on the surface of the semiconductor particle or in the liquid phase [6,7]. Hence, the primary as well as secondary reactions yield oxygen containing species of high reactivity such as hydroxyl radical ($\bullet OH$), superoxide radical anion ($O_2^{\bullet-}$), perhydroxyl radical (HO_2^{\bullet}), singlet oxygen molecule (1O_2) and hydrogen peroxide (H_2O_2). It has been proved that these reactive radicals and molecules are key species in mineralizing various organic compounds. It should be noted that direct UV photolysis of H_2O_2 can also lead to $\bullet OH$ formation [11]. The hydroxyl radical is often assumed to be the major reactant responsible for the photooxidation of organic molecules [10,12–15]. Due to the high reactivity and short lifetime (usually 10^{-9} s in a cell) [16] of $\bullet OH$ the direct detection of this species is difficult. Convincing evidences for the formation of $\bullet OH$ were obtained by photochemical and radiation chemical studies using various spin traps combined with transient absorption in UV-vis range and electron paramagnetic resonance (EPR) detection respectively [17–22]. Other methods such as steady state UV-vis absorption

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Scheme 1. Formation of 7-hydroxycoumarin in the reaction of coumarin with hydroxyl radicals.

[23], luminescence [24] and fluorescence [25–29], were also applied to measure the quantity of scavenged hydroxyl radicals. Recently, it has been proved that several non- or weakly-luminescent test molecules, such as terephthalic acid [30–35] and coumarin [36–40] produce strongly luminescent compounds with hydroxyl radical. Hence these molecules can be applied for detecting and measuring of ·OH radicals produced by radiation of homogeneous aqueous solution or by UV excitation of TiO₂ particles in heterogeneous systems. Ishibashi et al. [34] demonstrated that the fluorescence technique using terephthalic acid detects ·OH selectively over immobilized TiO₂ particles.

This article shows the results obtained by the fluorescence technique applying coumarin for the detection of ·OH radicals formed over TiO₂ surface exposed to UV light in aqueous suspension. Measurements have been carried out in aerobic and anaerobic conditions. In the latter case silver ion has been used as electron acceptor. The very efficient primary electron transfer from the conduction band of excited TiO₂ to silver ion leads to the deposition of Ag on TiO₂ surface [41]. This reaction does not produce radicals. Thus, a favorable and neat condition for transferring the hole to hydroxyl radical can be generated. To confirm that the free hydroxyl radical is required for formation of 7HC (see Scheme 1) oxalic acid as hole scavenger has been applied. This electron donor reactant, and the silver ion as electron acceptor have been used in aerobic conditions too for elucidating the details of the reactions resulting in the formation and then the disappearance of 7HC.

2. Experimental

2.1. Materials

TiO₂ used in experiments was obtained from Degussa (P25: 70% anatase, 30% rutile; surface area of 50 m² g⁻¹). Coumarin (COU) and 7-hydroxycoumarin (7HC) of the purest grade purchased from Sigma–Aldrich and Carlo Erba were used without further purification. All other reagents, such as oxalic acid, KMnO₄, AgNO₃ were purchased from Reanal (Hungary). Each chemical was dissolved in high purity water and used for the experiments. The high purity water was double distilled and then purified with the Milli-Q system.

2.2. Photoreactor and photocatalytic experiments

All experiments were carried out in a medium scale ($V = 2.8 \text{ dm}^3$) photochemical reactor. The reactor was developed for irradiation of heterogeneous reaction mixtures circulated by continuously fed air or other gases, such as Ar

as described earlier [41]. The flow rate of gases was 40 dm³ h⁻¹. The photon flux of the internal light source (40 W, $\lambda_{\text{max}} = 350 \text{ nm}$) was determined by potassium *tris*(oxalato)ferrate(III) chemical actinometry [42] and it was found to be $(6.95 \pm 0.04) \times 10^{-6} \text{ mol photon s}^{-1} \text{ dm}^{-3}$. The volume of the reaction mixture was set to be 2.8 dm³ prior to photolysis in all experiments. The initial concentration of coumarin was changed between 5×10^{-5} and $2 \times 10^{-3} \text{ M}$ during the preliminary experiments, then it was adjusted to 10^{-4} M as optimal value for most of the further experiments. The initial concentration of silver nitrate was varied from 0 to $2 \times 10^{-4} \text{ M}$. The concentration of TiO₂ was 1 g dm⁻³ in all experiments. The concentration of silver(I) was measured by the procedure described in details elsewhere [41]. The concentration of stock solution of oxalic acid (10^{-2} M) was checked by permanganometry and was used to prepare the reaction mixtures containing oxalic acid in various concentrations ($0\text{--}10^{-3} \text{ M}$).

2.3. Analytical procedures

Before and during the continuous illumination 5 cm³ samples were taken from the reaction mixture through a septum with a syringe. TiO₂-containing samples were filtered through a Millipore Millex-LCR PTFE 0.45 μm membrane filter. The fluorescence emission spectrum (excited at 332 nm) of 7-hydroxycoumarin was measured by a PerkinElmer LS 50B luminescence spectrometer. Both the emission and excitation slits were set to 5.0 nm during the measurements and the temperature of the solution was adjusted to 20.0 °C. Absorption spectra of coumarin, 7-hydroxycoumarin and the liquid phase of the reaction mixture was recorded by an Analytik Jena Model SPECORD S 100 spectrophotometer. The concentrations of 7-hydroxycoumarin formed and that of the coumarin disappeared were determined by using analytical measuring curves. These were obtained by plotting the luminescence intensity measured at 455 nm as a function of the concentration of the 7-hydroxycoumarin and the absorbance determined at 277 nm as a function of the concentration of COU respectively. The concentration of oxalic acid in the liquid phase of the reaction mixture was determined by classical permanganometry.

2.4. Adsorption measurements

These experiments were performed at neutral pH in dark. The stock solution of COU ($3 \times 10^{-3} \text{ M}$) was prepared by using high purity water then it was diluted to different concentrations ranged between 5×10^{-5} and 10^{-3} M . The concentration of COU in these homogeneous solutions was

checked by spectrophotometric method. 500 cm^3 of the solutions were transferred into a 750 cm^3 flask, then 500 mg TiO_2 was added to solutions. The suspensions were continuously stirred in dark and during this procedure 5 cm^3 samples were taken from time to time. The samples were filtered as given in Section 2.3 then the concentration of COU in the homogeneous solutions was measured by spectrophotometric method using cuvettes of suitable optical path. The concentration of COU in the aqueous phase decreased within 50 min then it was found to be constant. Moreover, the quantity of adsorbed COU was about 2.5% of the analytical concentration and $\text{COU}_{\text{ad}} = \{[\text{COU}]_T - [\text{COU}]_{\text{eq}}\}/C_{\text{TiO}_2}$ was found to depend almost linearly on $[\text{COU}]_T$ ($[\text{COU}]_T$ is the analytical concentration of COU, $[\text{COU}]_{\text{eq}}$ is the equilibrated COU concentration in the aqueous phase). The concentration of the photocatalyst was constant in all experiments ($C_{\text{TiO}_2} = 1\text{ g dm}^{-3}$). The results clearly indicated the weak adsorption of COU on Degussa P25 TiO_2 .

3. Results and discussion

3.1. Preliminary observations

To measure the yield of hydroxyl radical over photoexcited TiO_2 particles by fluorescence method using coumarin, Ishibasi et al. [34] proposed to use this radical scavenger in 10^{-4} to 10^{-3} M concentrations. Comparing the absorption spectra of COU with that of 7HC, and with the spectrum of the light source used in our photochemical experiments (Fig. 1) a considerable inner filter effect is expected, especially at high concentrations of radical scavenger.

In addition, as shown by our preliminary experiments, when homogeneous aqueous solution of COU is exposed to UV light, a slow disappearance of COU occurs, and a very small amount of luminescent species is formed (Fig. 2). Another experiment has demonstrated that 7HC completely disappears after 150 min photolysis using a reaction mixture of fluorescent compound in 10^{-6} M initial concentration and TiO_2 photocatalyst of 1 g dm^{-3} concentration (Fig. 3). Consequently, applying COU in relatively high concentrations to scavenge the

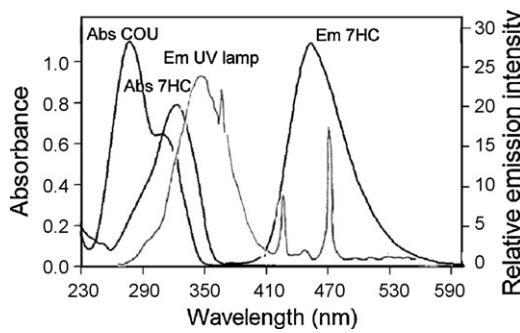


Fig. 1. Absorption (Abs 7HC) and fluorescence (Em 7HC) spectra of 7-hydroxycoumarin compared to absorption spectrum of coumarin (Abs COU) and the emission spectrum of the light source (Em UV lamp) used in our large-scale photoreactor. Concentration of 7HC was 5×10^{-5} and 7×10^{-7} M for absorption and fluorescence measurements respectively and concentration of COU was 10^{-4} M.

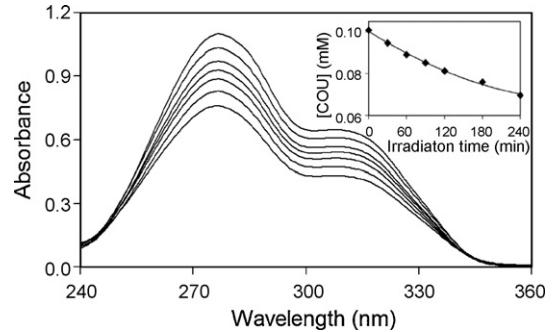


Fig. 2. Disappearance of coumarin under irradiation in its homogeneous aqueous solution: $[\text{COU}]_0 = 10^{-4}$ M, irradiation times: 0, 30, 60, 90, 120, 180 and 240 min.

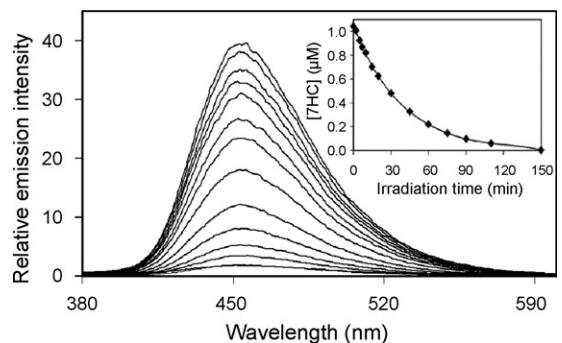


Fig. 3. The change of the luminescence spectrum of 7-hydroxycoumarin under its photolysis over TiO_2 particles: $[\text{7HC}]_0 = 10^{-6}$ M, and at 1 g dm^{-3} concentration of P25 photocatalyst.

hydroxyl radical, a significant fraction of incident light is absorbed by COU resulting in a decrease in the number of photons exciting the semiconductor particles. This inner filter effect leads to a significant decrease in the rate of 7HC formation.

On the other hand, at a low initial concentrations of COU it disappears rapidly upon irradiation. This process is accompanied by the formation of the fluorescent 7HC. Thus the concentration of this species would be comparable with that of the COU. Under these conditions 7HC can undergo either direct

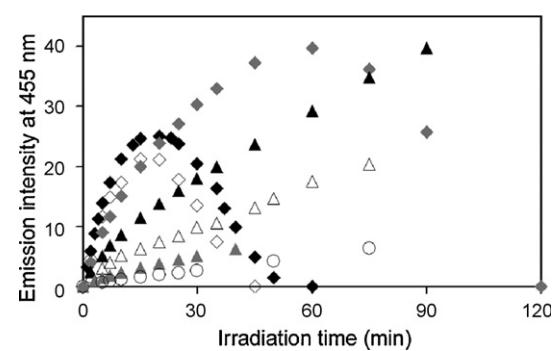


Fig. 4. The changes in emission intensity measured at 455 nm of the aqueous phase of the reaction mixture under heterogeneous photolysis of coumarin of various initial concentration: (\diamond) 5×10^{-5} M, (\blacklozenge) 10^{-4} M, (\blacklozenge) 3×10^{-4} M, (\blacktriangle) 5×10^{-4} M, (\triangle) 7×10^{-4} M and (\blacktriangle) 10^{-3} M, (\circ) 2×10^{-3} M.

Table 1

The initial rate of 7HC formation as function of initial concentration of COU

[COU] ₀ (M)	Initial form. rate ^a (M ⁻¹ s ⁻¹)
5 × 10 ⁻⁵	9.64 × 10 ⁻¹⁰
10 ⁻⁴	1.11 × 10 ⁻⁹
3 × 10 ⁻⁴	8.46 × 10 ⁻¹⁰
5 × 10 ⁻⁴	2.62 × 10 ⁻¹⁰
7 × 10 ⁻⁴	1.36 × 10 ⁻¹⁰
10 ⁻³	6.68 × 10 ⁻¹¹
2 × 10 ⁻³	3.64 × 10 ⁻¹¹

^a The initial formation rate of the fluorescent species was estimated by using a simple polynomial fitting to the luminescence intensity vs. irradiation time data measured at constant concentration of dissolved molecular oxygen as electron acceptor. The estimated error of initial formation rate is about 8%.

photolysis or TiO₂ assisted photodegradation. Hence, it is expected that the development of luminescence is followed by a leveling off, and finally the luminescence intensity decreases. The results of preliminary photolysis experiments (Fig. 4 and Table 1) clearly support these predictions.

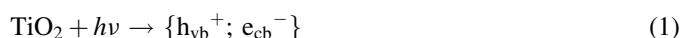
Fig. 4 and the data of Table 1 demonstrate that the feature of luminescence intensity vs. irradiation time curves and the initial formation rate of fluorescent species strongly depend on [COU]₀. The highest rate was obtained at 10⁻⁴ M initial concentration of COU. Hence, this concentration was preferred for further experiments.

3.2. Heterogeneous photolysis of coumarin in anaerobic conditions

The experiences shown in the previous section stimulated us to perform detailed studies on using coumarin for detecting and measuring hydroxyl radicals produced by UV excited TiO₂ particles. First, it has been confirmed that in the absence of any electron scavenger species, such as dissolved molecular oxygen and/or reducible metal ions like silver(I), the formation of 7HC is negligible. Fig. 5 demonstrates the time dependence of luminescence intensity originating from 7HC formed under irradiation at various initial concentration of silver(I).

A very small amount of photo-luminescent species has been detected under illumination of the Ar saturated reaction mixture of [Ag⁺] = 0. The formation of this species in such a low

concentration has been attributed to some residual oxygen or other impurities of electron acceptor properties in the suspension. Addition of silver ions to the system and by adjusting the initial silver concentration to 5 × 10⁻⁵ M leads to a rapid increase in the luminescence intensity, then this change is leveling off in a very short period, and after 10 min irradiation the intensity of the fluorescence signal remains constant. Under the first period, when the fluorescence intensity is evolved rapidly, the deposition of the silver to the surface of semiconductor particles also occurs. This is accompanied with a significant decrease in concentration of COU. When the luminescence intensity has achieved a constant value, silver ion is no longer detectable in the aqueous phase of suspension. The higher the initial silver ion concentration, the more luminescent species are formed. These experiences show that 7HC is formed only in the presence of efficient electron acceptor. Moreover, the luminescence intensity achieved at complete deposition of silver is proportional to the initial silver concentration. The electron constituents of {h_{vb}⁺; e_{cb}⁻} pairs are efficiently accepted by silver ions resulting in “free reactive holes” at the surface of the semiconductor particles. The number of these holes should be equivalent to that of deposited silver atoms. Hence, the relatively small ratio of the luminescent 7HC and the deposited silver ([7HC]/[Ag⁰] = 3.2 × 10⁻³) clearly demonstrates the low efficiency of the reaction pathways resulting in 7HC from holes. In principle, such a low yield of 7HC can be explained by efficient side reactions of •OH radicals occurring either at the surface of TiO₂ particle or in the liquid phase. It was pointed out by Nakamura et al. [43] that the main decay process of the surface trapped holes (h_{surf}⁺) or •OH radicals produced at the surface (•OH_{surf}), which species could not be distinguished, was the dimerization of •OH_{surf} radicals to form H₂O₂.



Since the redox potential of the surface trapped •OH is significantly lower (1.5 V [44]) than that of •OH in solution (1.9 V) and the adsorption of COU on the surface of TiO₂ is rather weak, it is reasonable to suppose that •OH_{surf} cannot react with COU. Thus, we assume that COU could probe only free •OH. This assumption is in accordance with the conclusion of Hirakawa et al. drawn from their study using terephthalic acid as fluorescent probe of hydroxyl radicals generated by photoexcitation of TiO₂ [35].

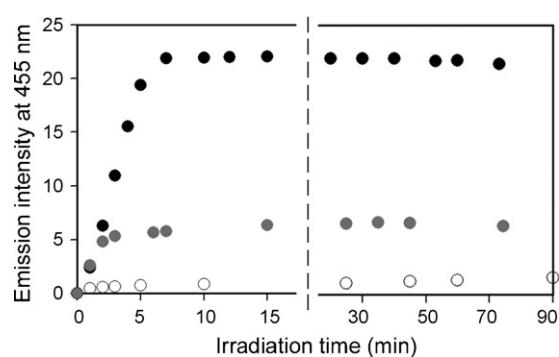
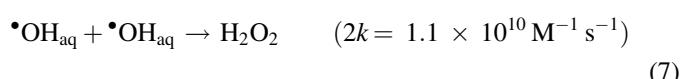
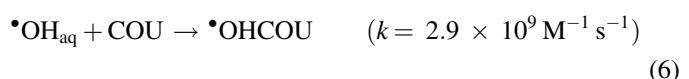


Fig. 5. Development of fluorescence measured at 455 nm in reaction mixture of 1 g dm⁻³ TiO₂, 10⁻⁴ M coumarin and various concentration of Ag⁺ under illumination: (○) [Ag⁺]₀ = 0 M, (●) [Ag⁺]₀ = 5 × 10⁻⁵ M and (●) [Ag⁺]₀ = 2 × 10⁻⁴ M.

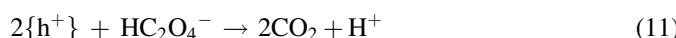
Under continuous irradiation the concentration of free hydroxyl radical should be very low related to the concentration of COU. Hence the yield of reaction (7) can be negligible in aqueous phase compared to that of reaction (6). A rather low yield of 7HC ($\sim 2.2 \times 10^{-4}$) has been estimated by comparing $[7\text{HC}]/[\text{Ag}^0] = 3.2 \times 10^{-3}$ value with the yield of silver deposition ($6.85 \times 10^{-2} \text{ Ag photon}^{-1}$), which can be explained by a significantly higher rate of reaction (4) than that of reaction (3).

The limiting fluorescence intensity obtained by Ar saturated reaction mixture using Ag^+ ions as electron scavenger ($[\text{Ag}^+]_0 = 2 \times 10^{-4} \text{ M}$) can be repressed by addition of sacrificial electron donor like oxalic acid. This is illustrated by Fig. 6.

The fluorescence intensity of 7HC achieved at the complete deposition of silver significantly decreases with increasing initial concentration of oxalic acid. The carbon dioxide radical anion is formed by primary electron transfer from HC_2O_4^- to the photogenerated hole (Eq. (8)). This radical can disappear in a bimolecular reaction, forming either hydrogen oxalate or carbon dioxide and formate ion via dismutation.



The formate ion is readily oxidized by two holes [45–46]. Hence it is expected that, if reaction (8) is followed by either reaction (9) or reaction (10) with the subsequent oxidation of formate, two holes are required to the complete oxidation of one HC_2O_4^- :



Thus the appearance of 7HC under illumination of the argon saturated reaction mixture containing $2 \times 10^{-4} \text{ M}$ silver ion, 10^{-4} M oxalic acid and 10^{-4} M coumarin is considered as an indication of the efficiency of reaction (3). Another plausible explanation would be the scavenging of $\cdot\text{CO}_2^-$ by coumarin;

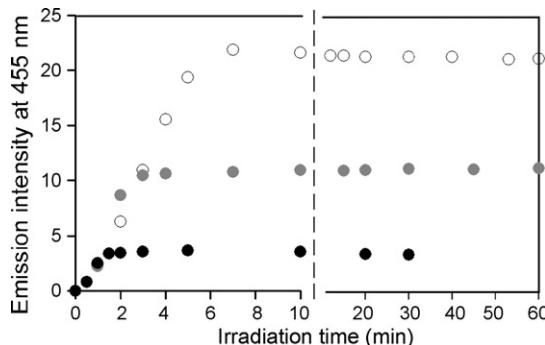


Fig. 6. Development of fluorescence measured at 455 nm in reaction mixture of $1 \text{ g dm}^{-3} \text{ TiO}_2$, 10^{-4} M coumarin, $[\text{Ag}^+]_0 = 2 \times 10^{-4} \text{ M}$ and various concentration of oxalic acid: (○) $[\text{Ox}]_0 = 0 \text{ M}$, (●) $[\text{Ox}]_0 = 10^{-4} \text{ M}$ and (●) $[\text{Ox}]_0 = 2 \times 10^{-4} \text{ M}$.

These assumptions are supported by the fact that the luminescent 7HC is formed even if the concentration of oxalic acid is $2 \times 10^{-4} \text{ M}$ (see Fig. 6).

3.3. Heterogeneous photolysis of coumarin in aerobic conditions

As it has been shown, heterogeneous photolysis of coumarin under anaerobic condition results in 7HC as luminescent final product. However, when the photolysis is carried out under aerobic conditions 7HC is formed as an intermediate (Fig. 4). In the latter case conduction band electron is trapped by oxygen resulting in superoxide radical $\text{O}_2^{\cdot-}$ while an electron is transferred from water molecule to the hole producing hydroxyl radical according to Eq. (3). Recent studies [9,16] as well as the results of our present investigations performed under anaerobic conditions have clearly demonstrated that $\cdot\text{OH}$ is responsible for the formation of 7HC. Thus the oxygen itself and/or the superoxide radical are the species that should play crucial role in the disappearance of 7HC. Fig. 7 shows that the initial formation rate of 7HC under anaerobic condition and that of in aerated suspension are very similar. In aerated suspension a leveling off occurs, then the luminescence intensity achieves a maximum value, and finally it is decreasing. It is remarkable that luminescence signal cannot be detected after 60 min irradiation.

Representative results of photocatalytic experiments carried out under aerobic conditions using oxalic acid as hole scavenger in various concentrations ($0 < [\text{Ox}]_0 < 10^{-3} \text{ M}$) are illustrated by Fig. 8.

Addition of oxalic acid to the reaction mixture ($[\text{COU}]_0 = 10^{-4} \text{ M}$ and $1 \text{ g dm}^{-3} \text{ TiO}_2$) leads to a significant delay in the appearance of the fluorescence signal. It clearly indicates that the efficient electron donors such as oxalic acid, which can directly transfer electron to the photogenerated hole, hinder the formation of fluorescent 7HC. It should be noted that a delay in the evolution of luminescence follows even at rather low initial concentration of hole scavenger (e.g. $[\text{Ox}]_0 = 6 \times 10^{-5} \text{ M}$). The higher the hole scavenger concentration the longer delays are detected. It is important to note that

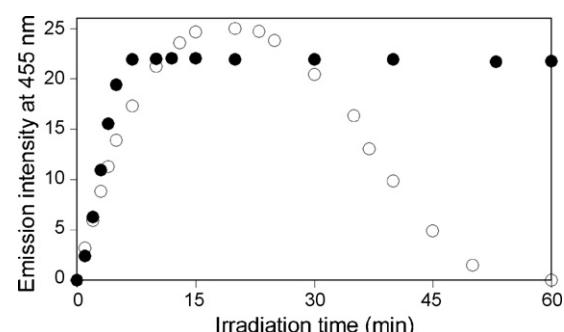


Fig. 7. Comparison of the change of luminescence intensities attributed to 7HC under irradiation of reaction mixtures under aerobic (○) and anaerobic (●) conditions. $[\text{COU}]_0 = 10^{-4} \text{ M}$ for both measurements, $[\text{O}_2] = (2.8 \pm 0.1) \times 10^{-4} \text{ M}$ for (○) and $[\text{Ag}^+]_0 = 2 \times 10^{-4} \text{ M}$ for (●).

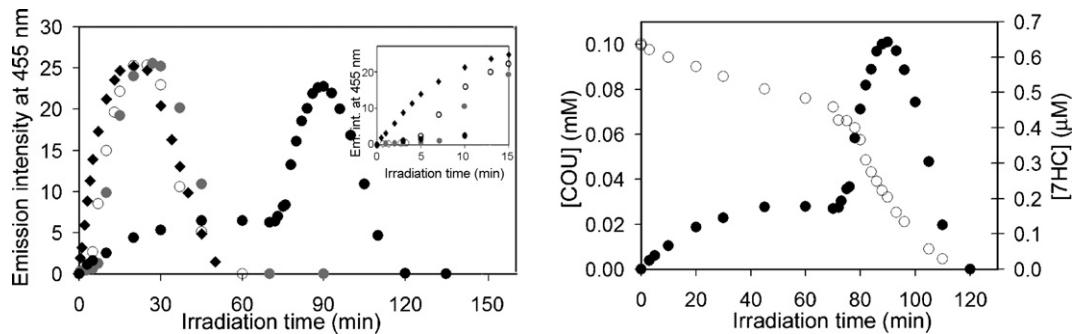
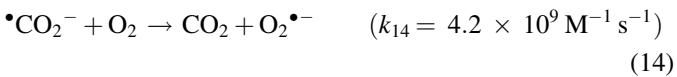


Fig. 8. Change of the fluorescence intensity measured at 455 nm upon illumination of reaction mixture of 1 g dm^{-3} TiO_2 , 10^{-4} M coumarin and various concentration of oxalic acid: (\blacklozenge) $[\text{Ox}]_0 = 0 \text{ M}$, (\circ) $[\text{Ox}]_0 = 6 \times 10^{-5} \text{ M}$, (\bullet) $[\text{Ox}]_0 = 10^{-4} \text{ M}$ and (\bullet) $[\text{Ox}]_0 = 10^{-3} \text{ M}$ and at constant oxygen concentration. Inset shows the luminescence intensities within 15 min irradiation. (left) Change in concentrations of COU (\circ) and 7HC (\bullet) in aqueous suspension of COU, Ox and TiO_2 (g dm^{-3}) under illumination: $[\text{COU}]_0 = 10^{-4} \text{ M}$ and $[\text{Ox}]_0 = 10^{-3} \text{ M}$. (right).

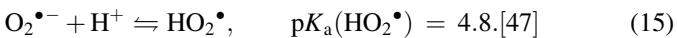
the rate of the fluorescence development after the inhibition period is identical with that of observed at $[\text{Ox}]_0 = 0 \text{ M}$. The explanation of these observations is that oxalic acid adsorbed on the surface of TiO_2 significantly suppresses the formation of free hydroxyl radical and thus the hydroxylation of COU. The inhibition period is finished at the complete oxidation of the oxalic acid to CO_2 . Regarding the fate of CO_2^- , it is expected that various reactions can undergo to oxidize it to CO_2 by one-electron transfer processes. As it has been demonstrated in Section 3.2, a very efficient scavenging of e_{cb}^- provides rather high concentration of hole. These holes may also oxidize CO_2^- .



However, this process is negligible when the concentration of HC_2O_4^- is high (e.g. 10^{-3} M) and the holes are (almost) completely consumed by the electron transfer from the oxalate ions. Since the concentration of adsorbed oxygen is constant in the reaction mixture ($\sim 2 \times 10^{-4} \text{ M}$ in the liquid phase) and it is significantly higher than the quasi stationer concentration of CO_2^- , it is reasonable to suppose that the radical–radical reactions (Eqs. (9)–(10)) and reaction (13) can be negligible related to reaction (14).

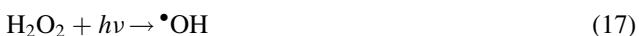


The superoxide radical anion is protonated at pH values of our experiments.

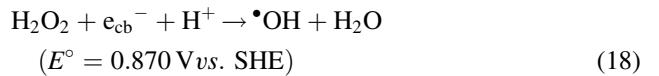


It is important to note that hydroxyl radicals can be generated by the reactions of $\text{HO}_2\cdot$ formed either by electron transfer from conduction band to molecular oxygen, or by secondary reaction of CO_2^- with different pathways:

(a)

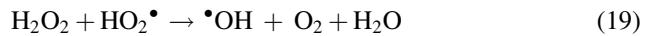


(b) Reactions (5) or (7) and (16) are followed by



or by

(c)



So, instead of by the direct electron transfer from water to photogenerated hole (Eq. (3)), hydroxyl radicals are produced by secondary reactions through various pathways (a–c above) at high oxalic acid concentrations (e.g. 10^{-3} M) as demonstrated by Fig. 8. Under this condition the fluorescence intensity of photoexcited 7HC increases moderately, then it is leveling off, and finally it is slightly decreased. However when the oxalic acid has been completely oxidized to CO_2 a characteristic change is observed. Namely, the luminescence intensity starts to increase with a rate which is similar to that of experienced at the initial stage of the photolysis in reaction mixture containing no oxalic acid. The remarkable feature of the luminescence intensity vs. irradiation time curves is that the fluorescence intensity starts to increase rapidly when the consumption of oxalic acid has been completed, which is resembling to an end point of a titration using fluorescence indication. Upon illumination the concentration of COU decreases with a moderate rate, which is leveling off slowly under photooxidation of oxalic acid. Then, its rapid decomposition starts due to the efficient formation of hydroxyl radical after the complete decomposition of oxalic acid. These findings confirm that:

- The coumarin is effectively attacked by hydroxyl radical, on the other hand its direct reaction with other oxygen containing radical such as, $\text{HO}_2\cdot$ is negligible.
- Oxygen itself and oxygen containing radicals play crucial role in the further reaction of the hydroxylated COU radical producing 7HC and the fragmentation of COU/7HC.
- In the presence of oxalic acid in concentrations over than 10^{-5} M the steady state concentration of free $\cdot\text{OH}$ radicals is low for efficient hydroxylation of COU.

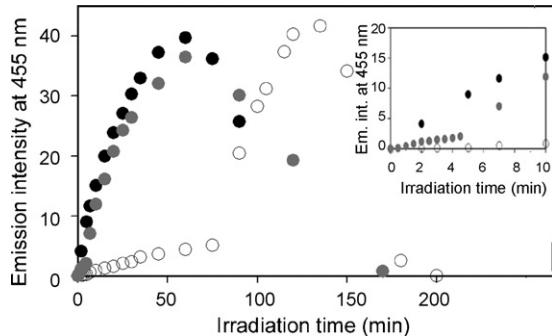


Fig. 9. Change of the fluorescence intensity measured at 455 nm upon illumination of reaction mixture of 1 g dm^{-3} TiO_2 , $3 \times 10^{-4} \text{ M}$ coumarin and various concentration of oxalic acid and silver (I) ion: (●) $[\text{Ox}]_0 = 0 \text{ M}$, $[\text{Ag}^+]_0 = 0 \text{ M}$, (●) $[\text{Ox}]_0 = 2 \times 10^{-4} \text{ M}$, $[\text{Ag}^+]_0 = 2 \times 10^{-4} \text{ M}$ and (○) $[\text{Ox}]_0 = 10^{-3} \text{ M}$, $[\text{Ag}^+]_0 = 0 \text{ M}$.

(d) The primary electron transfer from the oxalic acid (or oxalate ion) is followed by thermal redox reactions resulting in hydroxyl radicals too.

3.4. The effect of silver ions in the presence of oxalic acid in aerobic conditions

The influence of a sacrificial electron donor like oxalic acid and the simultaneous effect of electron donor and electron acceptor such as Ag^+ are compared by Fig. 9. It should be noted that the initial concentration of COU was adjusted to $3 \times 10^{-4} \text{ M}$ in these experiments. Thus, 7HC has been formed with somewhat smaller rate than that of observed using COU of 10^{-4} M initial concentration, due to the enhanced inner filter effect as discussed in Section 3.1. Moreover, the maximum of the luminescence intensity has been achieved at 60 min irradiation which is about three times longer period than that of detected in experiments performed by 10^{-4} M initial concentration of COU (Fig. 8). The inhibition period caused by oxalic acid of 10^{-3} M in 7HC formation is slightly longer than that of observed at $[\text{COU}]_0 = 10^{-4} \text{ M}$, which is a further consequence of the enhanced inner filter effect of COU of $3 \times 10^{-4} \text{ M}$.

The simultaneous application of oxalic acid and silver results in a relatively short inhibition period with a more rapid formation of 7HC than in experiment using only oxalic acid. This finding is reasonably explained by the enhanced photooxidation rate of oxalic acid under silver deposition and over silver deposited TiO_2 [41], that leads to a significant increase in the yield of hydroxyl radical produced by reaction pathways; (a) (8) (14) (15) (16) and (17), (18) or (19), and (b) electron scavenging by oxygen at the surface of TiO_2 particle followed by (15) (16) and (17), (18) or (19).

4. Conclusions

Applicability of coumarin as fluorescent probe for detecting and measuring of hydroxyl radicals generated by excitation of TiO_2 nanoparticles in various conditions has been studied. It has been demonstrated that sacrificial electron acceptors are required to obtain luminescent 7HC in illuminated aqueous

suspension of TiO_2 . In argon saturated suspension the luminescent 7HC is rapidly formed when silver ion is used to scavenge the photogenerated electron (e_{cb}^-). When the reduction of silver ions has been completed and hence the silver clusters have been deposited on the surface of TiO_2 particles the formation of 7HC is stopped. The luminescence intensity detected at this stage of photolysis linearly depends on the initial concentration of silver ions. Thus, the quantum yield of 7HC formation is measurable with a high accuracy by this method. It is important to note that the yield of 7HC is considerably lower than the yield of deposited silver. When dissolved oxygen is used as electron acceptor and its constant concentration is adjusted by continuous fed of air, 7HC appears as an intermediate of heterogeneous photolysis of COU.

The inner filter effect of COU has also been demonstrated. So, a careful preliminary experiment to optimize the conditions of using coumarin for measuring hydroxyl radicals is recommended. It has also been shown that coumarin can be applied as a fluorescent indicator of complete photoconversion of sacrificial electron donor compounds such as oxalic acid.

Using net one electron acceptors such as silver ion and sacrificial electron donor, e.g. oxalic acid proved to be a powerful technique to deepen our knowledge on reactions induced by photoexcited semiconductor nanoparticles.

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